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(54) **Core-shell polymer, production and use thereof**

Kern-Schale-Polymer, Herstellung und dessen Verwendung

Polymère coeur-enveloppe, production et son utilisation

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EP-A- 0 265 142

GB-A- 2 091 744

GB-A- 2 196 011

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US-A- 4 556 690

US-A- 4 639 488

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Description

The present invention relates to a core-shell polymer, a method of producing said core-shell polymer and its use as an impact modifier for polyoxymethylene resins.

[Background of this invention]

Polyoxymethylene (POM) resin has recently been used as a molding material for various end products (such as gears and reels) but the molded articles manufactured from this resin are not fully satisfactory in impact strength, thus setting many attempts going to improve POM in this respect.

However, for chemical structural reasons, POM resin has had no partner resin that is sufficiently compatible with it. Furthermore, POM resin is not thermally stable and, therefore, not suited for high-temperature blending.

A variety of core-shell polymers have been proposed for incorporation in many thermoplastic resins by the melt-blending technique for the purpose of, in the main, improving the impact strength of the final resin. Among them, a core-shell polymer comprising a rubbery polymer core and a glassy polymer shell has the advantage that its dispersibility is less sensitive to variations in melt-blending conditions and hence it can be uniformly dispersed with high reproducibility. These core-shell polymers are used as an impact modifier for polycarbonate, poly(butylene terephthalate), polyamide, polyphenyleneoxide and their mixture, polymer alloy.

However, the prior art core-shell polymers have the disadvantage that the core-shell polymer contains the ingredient which promotes thermal decomposition of POM, due to drawbacks in the methods employed for their synthesis. Therefore, they can hardly be evenly blended with POM resin. Furthermore, even if they could be blended with POM resin more or less successfully, the resulting compositions are poor in thermal stability.

EP-A-0 115 373 discloses a POM resin composition containing a rubbery elastomer obtainable on emulsion polymerization of an C_{1-8} alkyl acrylate but as the special blending conditions are indicated therein, a fully stable POM resin composition is hard to come by under the ordinary blending conditions. Moreover, the composition is not improved on its thermal stability because of no consideration at the emulsion polymerization.

U.S.P. 4,713,414 discloses a POM resin composition containing core-shell polymers and reactive titanate. But this core-shell polymer also contains impurities decomposing POM resin. Therefore, a stable POM resin composition cannot be produced. A comparative example between core-shell polymers of this invention and of U.S.P. 4,713,414 and EP-A-0 115 373 is disclosed as a comparative example 1 in this application.

As a POM resin composition assuring an improved impact strength, the composition proposed in U.S.P. 4,804,716 is known. While it is a POM resin composition capable of forming a thermoplastic IPN (interpenetrating polymer network) with a polyurethane elastomer, assurance of sufficiently high impact strength calls for the use of a fairly large amount of polyurethane elastomer which should detract considerably from the modulus of the molded article, let alone the disadvantages of inadequate thermal stability and fluidity.

U.S.P. 4,639,488 discloses a POM resin composition containing a rubbery elastomer obtainable by emulsion polymerization of butadiene but this composition is also lacking in thermal stability.

U.S.P. 3,749,755 discloses a POM resin composition containing a rubbery grafted elastomer. But this composition is lacking in thermal stability and the rubbery grafted elastomer is not described as a core-shell polymer.

Japanese Patent Examined No. 15331/1984 discloses a method for producing a thermoplastic resin like acrylonitrile-acrylate-styrene (AAS resin) using emulsion polymerization technique improved on impact strength. This is, however, copolymer not a blend mixture.

EP-A-0 305 273 discloses a method of preparation for latex using non-ionic surfactant. This latex, however, is used to be toughen a vinyl polymer, and is not a core-shell polymer.

GB-A-2 196 011 discloses a graft copolymer consisting of a rubbery core and a hard shell produced by preparing the rubbery core by polymerizing butadiene and styrene, using the emulsion polymerization method. Said emulsion polymerization method is conducted in the presence of an anionic emulsifier, preferably potassium oleate.

Further, EP-A-0 265 142 discloses a core/shell polymer comprising a rubbery core of crosslinked, conjugated diolefin polymer or copolymer and one or more polymer shells, at least one of which shells is a vinylaromatic polymer or copolymer. Again the polymerization is conducted in the presence of the anionic emulsifier potassium oleate.

Polymer blend composed of crystalline polymer has the defect that it has low strength and elongation on the weld line. POM is the highly crystalline polymer. Therefore, the POM composition incorporated with polyurethane elastomer in order to improve impact strength shows much lower strength and elongation on the weld line than neat POM.

Moreover, POM has not good weatherability among engineering plastics. The POM composition incorporated in particular with polyurethane elastomer shows much inferior weatherability.

The present inventors have made intensive investigations to improve impact strength, thermal stability, strength and elongation on the weld line, and weatherability of POM composition. From the investigation, they have found that the POM composition comprising a certain core-shell polymer shows much higher impact strength and better weath-

erability than the neat POM. The POM composition also has improved thermal stability, and strength and elongation on the weld line.

[Detailed description of this invention]

The present inventors conducted an intensive and diligent research for developing a core-shell polymer capable of providing a POM resin composition with improved impact strength and discovered that the polymerization initiator and surfactant heretofore used in the polymerization reaction exert adverse effects on the thermal stability of POM resin.

After further investigation, they discovered that the above-mentioned disadvantage can be overcome by incorporating a core-shell polymer having the under-mentioned structure in the resin composition and accordingly completed the present invention.

The present invention relates to a core-shell polymer obtainable by seeded emulsion polymerizing a core of a conjugated diene or a C_{2-8} alkylacrylate or a mixture thereof and a shell of methyl methacrylate and a monomer copolymerizable therewith according to the method of claim 1 comprising a rubbery polymer core and a glassy polymer shell characterized in that it has no detectable anion by

(a) the method which comprises stirring 5 g of the core-shell polymer in 20 ml of distilled water for 3 hours at room temperature, adding 0.1 ml of 1% barium chloride aqueous solution to the extracted sample solution, and observing whether precipitation appeared or not, or

(b) the method which comprises stirring 5 g of the core-shell polymer in 20 ml of distilled water for 3 hours at room temperature, adding 0.5 ml of 0.1 N silver nitrate aqueous solution to the extracted sample solution, and observing whether precipitation appeared or not.

The core-shell polymer of the invention is produced by seeded emulsion polymerization which method is performed by

(a) feeding a mixture of a conjugated diene or a C_{2-8} alkyl acrylate or a mixture thereof and/or a monomer copolymerizable therewith and a nonionic surfactant in water into a reactor, adding a polymerization initiator which liberates neutral radicals and emulsion polymerizing said mixture to obtain a rubbery polymer core,

(b) feeding a mixture of a methyl methacrylate and a monomer copolymerizable therewith and a nonionic surfactant into the reactor, adding a polymerization initiator which liberates neutral radicals and emulsion polymerizing composition to obtain a core-shell polymer;

wherein the glass transition temperature of the rubbery core phase is not more than -30°C and the glass transition temperature of the glassy shell phase is not less than 60°C . In this core-shell polymer, no anion can be detected by the usual anion detection technique.

For examples of methods for detecting anion include a method comprising stirring 5 g of core-shell polymers in 20 ml of distilled water for 3 hours at room temperature, filtrating the core-shell polymer solution to obtain filtrate, dividing the filtrate into two parts of the same volume, adding 0.1 ml of 1% barium chloride aqueous solution into one part of the filtrate and comparing the solution with another filtrate. If sulfate anion is contained in the filtrate, precipitate was observed in the solution added barium chloride into.

Another method comprises stirring 5 g of core-shell polymers in 20 ml of distilled water for 3 hours at room temperature, filtrating the core-shell polymer solution to obtain filtrate, dividing the filtrate into two parts of the same volume, adding 0.5 ml of 0.1 N silver nitrate aqueous solution into one part of the filtrate and comparing the solution with another filtrate. If halogen anion is contained in the filtrate, precipitate was observed in the solution added silver nitrate into.

An anion such as metal carboxylate, can be also detected by a conventional method. In this invention the core-shell polymer is substantially free from an anion such as metal carboxylate.

Furthermore, the present invention relates to the use of the above core-shell polymer or the core-shell polymer obtained by the above method as an impact modifier for polyoxymethylene resins.

In accordance with the invention, the emulsion polymerization is conducted using, for example, the following surfactant and polymerization initiator.

With regard to the surfactant, a large majority of the nonionic surfactants in common use can be utilized. Thus, for example, nonionic surfactants of the ether type such as polyoxyethylene nonylphenyl ether, polyoxyethylene stearyl ether and polyoxyethylene lauryl ether, nonionic surfactants of the ester type such as polyoxyethylene monostearate, nonionic surfactants of the sorbitan ester type such as polyoxyethylene sorbitan monolaurate, and nonionic surfactants of block copolymer type such as polyoxyethylene polyoxypropylene block copolymer, may be mentioned. The level of addition of the surfactant is chosen according to the particle-stabilizing activity of the surfactant. The surfactants used in Examples of this application are preferably used. More preferably polyoxyethylene nonylphenylether is used.

Since those surfactants are nonionic, they do not liberate anions, thus little causing POM resin to be decomposed.

With regard to the polymerization initiator which liberates neutral radicals, there may be employed initiators of the azo type, such as azobis(isobutyronitrile), dimethyl 2,2'-azobis(isobutyrate), and 2,2'-azobis(2-amidinopropane)-2HCl and peroxides such as cumene hydroperoxide, diisopropylbenzene hydroperoxide and hydrogen peroxide.

5 All of these polymerization initiators do not introduce anions into the terminals of the product core-shell polymer, thus little decomposing the POM resin. Preferably an initiator of azo type and of peroxide type are used.

Thus, when the emulsion polymerization is carried out in a reaction system using an anion-free surfactant and an anion-free polymerization initiator, the resulting core-shell polymer is also definitely free of anion. This core-shell polymer free of anion is preferred. In other aspect, a core-shell polymer having a few anion of which amount cannot be detected by the method mentioned above can be used in this invention.

10 The POM resin composition prepared using such a core-shell polymer is excellent in impact strength.

The core-shell polymer according to this invention is produced by the seeded emulsion polymerization technique which is a serial multi-stage emulsion polymerization process such that the polymer formed in a preceding stage is successively covered with a polymer formed in a later stage.

15 For producing the seed of the emulsion polymerization, the preferred procedure comprises mixing the monomer, surfactant and water, feeding the mixture to a reactor and adding the polymerization initiator. In other words, the monomer droplets are preferably comminuted beforehand.

The above pretreatment may, for example, be effected using a disperser or homogenizer until the mixture of monomer, surfactant and water is sufficiently emulsified.

20 The first-stage polymerization is a reaction giving rise to a rubbery polymer.

As the monomer forming said rubbery polymer, a conjugated diene or a C₂₋₈ alkyl acrylate, or a mixture thereof can be mentioned.

The above monomer or monomers are polymerized to give a rubbery polymer with a glass transition temperature not over -30°C.

25 While butadiene, isoprene and chloroprene can be mentioned as examples of the conjugated diene, butadiene is particularly advantageous.

As examples of the C₂₋₈ alkyl acrylate, there may be mentioned ethyl acrylate, propyl acrylate, butyl acrylate, cyclohexyl acrylate and 2-ethylhexyl acrylate, although butyl acrylate is particularly preferred.

30 In the first-stage polymerization, the conjugated diene and/or alkyl acrylate may be copolymerized with other comonomers such as aromatic vinyl or vinylidene monomers, e.g. styrene, vinyltoluene and α -methylstyrene, vinyl or vinylidene cyanides, e.g. acrylonitrile, methacrylonitrile, and alkyl methacrylates, e.g. methyl methacrylate and butyl methacrylate.

35 In case the first-stage polymerization system does not involve a conjugated diene or, if does, involves it only in a proportion of not more than 20 weight % of the total first-stage monomer charge, a high impact strength can be realized by using small amounts of a crosslinking monomer and a grafting monomer.

40 Examples of the crosslinking monomer include aromatic divinyl monomers such as divinylbenzene, alkane polyol polyacrylates and alkane polyol polymethacrylates such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, butylene glycol diacrylate, hexanediol diacrylate, hexanediol dimethacrylate, oligoethylene glycol diacrylate, oligoethylene glycol dimethacrylate, trimethylolpropane diacrylate, trimethylolpropane dimethacrylate, trimethylolpropane triacrylate and trimethylolpropane trimethacrylate. Particularly preferred are butylene glycol diacrylate and hexanediol diacrylate.

Examples of the grafting monomer include unsaturated carboxylic acid allyl esters such as allyl acrylate, allyl methacrylate, diallyl maleate, diallyl fumarate and, diallyl itaconate. Particularly preferred is allyl methacrylate.

45 The crosslinking and grafting monomers mentioned above are each used in the range of 0.01 to 5 weight %, preferably 0.1 to 2 weight %, based on the total weight of the first-stage monomer charge.

This rubbery polymer core phase preferably accounts for 50 to 90 weight % of the total core-shell polymer. If the proportion of the rubbery core phase is either less or more than the above limits, the resin composition prepared by melt-blending of the core-shell polymer may not have been fully improved in impact strength.

50 If the glass transition temperature of the rubbery core phase is higher than -30°C, the improvement in low-temperature impact strength may not be as great as desired.

The outer shell phase is constituted by a glassy polymer.

As examples of the monomer forming this glassy polymer, there may be mentioned methyl methacrylate and various monomers copolymerizable with methyl methacrylate.

55 This monomer is either methyl methacrylate or a mixture of methyl methacrylate and one or more monomers copolymerizable therewith, and forms a glassy polymer with a glass transition temperature of not less than 60°C.

Examples of the monomers copolymerizable with methyl methacrylate include alkyl acrylates such as ethyl acrylate and butyl acrylate, alkyl methacrylates such as ethyl methacrylate and butyl methacrylate, aromatic vinyl or vinylidene monomers such as styrene, vinyltoluene and α -methylstyrene, and vinyl or vinylidene cyanides such as acrylonitrile

and methacrylonitrile. Particularly preferred are ethyl acrylate, styrene and acrylonitrile.

The outer shell phase preferably accounts for 10 to 50 weight % of the total core-shell polymer. If the proportion of this outer phase is more or less than the above limits, the resin composition obtainable by melt-blending the resulting core-shell polymer with POM resin may not have been sufficiently improved in impact strength.

Further, the core-shell polymer may have an intermediate phase between the first rubbery polymer phase and the outer glassy polymer phase. The polymerization for the intermediate phase can be carried out by a method of emulsion polymerization. For example, the intermediate phase can be obtained by polymerizing one or more monomers selected from the group of polymerizable monomers having a functional group such as glycidyl methacrylate, unsaturated carboxylic acid, polymerizable monomers for a glassy polymer such as methyl methacrylate and styrene, and polymerizable monomers for a rubbery polymer such as butyl acrylate and butadiene. The monomer for polymerization of the intermediate phase can be suitably selected according to its property.

An amount of the intermediate phase can be also suitably selected according to the polymerized monomer. For example, in the case that the intermediate phase is a glassy polymer, its amount can be calculated as a part of shell phase. In another case that the intermediate phase is a rubbery polymer, its amount can be calculated as a part of core phase.

The structures of the core-shell polymer having an intermediate phase are exemplified as a multi-layers structure or a salami-type structure. While a core-shell polymer has a multi-layers structure, it contains at least 3 layers, such as a core layer, an intermediate layer on the core layer and a shell layer on the intermediate layer. In another case that a core-shell polymer has a salami-type structure, the intermediate phase is embedded and is dispersed in the core layer in the form of small particles. In the excessive case that a core-shell polymer has a salami-type structure using the monomer represented by styrene for the intermediate phase, the intermediate phase embedded in a core phase cannot be dispersed and becomes the center layer in the core layer. In this invention any type of core-shell polymer can be used.

The flexural modulus, the heat-distortion temperature, the appearance (the change of chromaticity by refractive index and the suppression of delamination and parlescense) can be improved by using the core-shell polymer having the intermediate phase.

The core-shell polymer obtained by the method mentioned above has 100 to 1,000 nm of an average diameter. Preferably its range is from 120 to 600 nm. The core-shell polymer having the range mentioned above of the diameter is convenient.

The core-shell polymer of the invention can be obtained in the form of granules, flakes or powders for example by the following procedures.

(1) Using the aforesaid surfactant and polymerization initiator, a latex is prepared by the seeded emulsion polymerization method which is known per se.

(2) This latex is subjected to freeze-thaw treatment to separate the polymer.

(3) The polymer is centrifugally dehydrated and dried.

By the above separation procedures, most of the surfactant used in the emulsion polymerization step can be removed.

The latex obtained in step (2) can be directly dried and used as it is.

Spray-drying using a spray dryer is also a method for separating the core-shell polymer from the latex.

The core-shell polymer thus separated can be processed into pellets by means of an extruder and a pelletizer, or can be directly melt-blended into the resin and as it is.

The POM resin of the invention is a melt-blended mixture of 100 parts by weight of POM resin and 5 to 100 parts by weight, preferably 10 to 80 parts by weight, of the above core-shell polymer.

If the proportion of the core-shell polymer is less than 2 parts by weight, the resulting resin composition may not have been improved in impact strength, while the use of the core-shell polymer in excess of 100 parts by weight may result in considerable decreases in rigidity and heat resistance of the final resin composition.

The POM resin to be used in accordance with the invention includes, among others, a homopolymer of formaldehyde and a copolymer of either formaldehyde or a cyclic oligomer thereof with an oxylalkylene compound containing at least two adjacent carbon atoms in the backbone chain, and any of polyoxymethylene homopolymer and polyoxymethylene copolymer resins can be successfully employed.

For the production of the POM resin of the invention, the melt-blending technique is employed.

The melt-blending is generally carried out at an appropriate temperature between 18° and 240°C, where the resin melts and the viscosity of the melt is not too low.

The melt-blending can also be carried out by means of a heating roll, a Bambury mixer or a single-screw or multi-screw extruder.

Furthermore, the resin composition of the invention may contain various additives and other resins in appropriate

proportions.

Among such additives are flame retardants, mold-releases, weathering stabilizers, antioxidants, antistatic agents, heat builders, colors, reinforcements, surfactants, inorganic fillers and lubricants.

The core-shell polymer of the invention provides for markedly improved impact strength when melt-blended with the POM resin.

Furthermore, the resin containing the core-shell polymer of the invention is superior to comparable resins containing the known core-shell polymer used as an impact modifier in thermal stability and to the resin composition containing an urethane elastomer in fluidity, thermal stability, strength and elongation on the weld line, weatherability and an appearance.

The strength and elongation on the weld line are improved in this invention.

[Examples]

The following examples and comparative examples are intended to illustrate the invention in further detail and should by no means be construed as limiting the metes and bounds of the invention. It should be understood that in these examples and comparative examples, all parts are by weight and the following abbreviations are used.

n-Butyl acrylate	BA
Ethyl acrylate	EA
Methyl methacrylate	MMA
Vinyl acetate	VAc
Butadiene	Bd
Glycidyl methacrylate	GMA
2-Ethylhexyl acrylate	2EHA
Hydroxyethyl methacrylate	HEMA
Allyl methacrylate	A1MA
1,4-Butylene glycol diacrylate	BGA
Deionized water	DIW
Polyoxyethylene nonylphenyl ether (Emulgen® 950, Kao Corporation)	E950
Polyoxyethylene nonylphenyl ether (Emulgen® 985, Kao Corporation)	E985
Polyoxyethylene lauryl ether (NOIGEN® YX-500, Dai-ichi Kogyo Seiyaku Co. Ltd.)	YX500
Polyoxyethylene monostearate (Nonion® S-40, Nippon Oil & Fats Co. Ltd.)	S40
Polyoxyethylene sorbitan monolaurate (Nonion® LT-221, Nippon Oil & Fats Co. Ltd.)	LT221
Polyoxyethylene polyoxypropylene block polymer (Epan® 785, Dai-ichi Kogyo Seiyaku Co. Ltd.)	EPN
Sodium octylsulfosuccinate (Neocol® P, Dai-ichi Kogyo Seiyaku Co. Ltd.)	NP
Sodium hydrogen carbonate	SBC
2,2'-Azobis(methylisobutyrate) (V601, Wako Pharm. Corp.)	V601
2,2'-Azobis(2-amidinopropane)-HCl (V50, Wako Pharm. Corp.)	V50
Hydrogen peroxide	H ₂ O ₂
Vitamin C (ascorbic acid)	VC
Sodium persulfate	SPS

Example 1 Production of core-shell polymer A

A 5-liter polymerization vessel equipped with a reflux condenser was charged with 1125 g of DIW and 135 g of a 10% aqueous solution of E950 and the mixture was stirred under a nitrogen stream and heated to 70°C. On the other hand, 90 g of a first-stage monomer mixture of the under-mentioned composition was mixed with 45 g of a 10% aqueous solution of E950 and 90 g of DIW and the mixture was fully emulsified with a disperser. The resulting emulsion was added to the above reaction mixture and dispersed for 10 minutes. Then, 3.6 g of V601 was added for polymerization

of seed latex.

First-stage monomer	
BA	1792.8 g
A1MA	3.6 g
BGA	3.6 g

The remaining 1710 g portion of the first-stage monomer mixture was mixed with 1500 g of a 10% aqueous solution of E950 and 525 g of DIW and the resulting monomer emulsion was continuously fed over a period of 250 minutes for seeded polymerization.

The reaction mixture was heated to 90°C and kept for one hour, then cooled to 70°C for second-stage polymerization.

Thus, 1.5 g of V601 was added and 1125 g of a second-stage monomer emulsion of the under-mentioned composition was continuously fed over a period of 200 minutes for seeded polymerization.

Second-stage monomer emulsion	
MMA	405.0 g
EA	45.0 g
E985, 10% aqueous solution	362.0 g
DIW	313.0 g

The reaction mixture was heated to 90°C and kept for one hour then, cooled and filtered through a 300-mesh stainless steel sieve to give a core-shell polymer latex.

This latex was frozen at -15°C and filtered through a glass filter. The solid was then dried in a current of air at 60°C overnight to give core-shell polymer A.

Example 2 Production of core-shell polymer B

A 5-liter polymerization vessel equipped with a reflux condenser was charged with 1320 g of DIW and 66 g of a 10% aqueous solution of E950 and the mixture was stirred under a nitrogen stream and heated to 70°C. 77 g of a first-stage monomer mixture of the under-mentioned composition was added to the above mixture and dispersed for 10 minutes. Then, 154 g of a 2% aqueous solution of V50 was added for polymerization of seed latex.

First-stage monomer	
BA	1533.84 g
A1MA	3.08 g
BGA	3.08 g

The remaining 1463 g portion of the first-stage monomer mixture was mixed with 440 g of a 10% aqueous solution of E950 and 440 g of DIW, and the resulting monomer emulsion was continuously fed over a period of 180 minutes for seeded polymerization.

The reaction mixture was kept for one hour at 70°C, and was subject to the second-stage polymerization.

Thus, 66 g of a 2% aqueous solution of V50 was added and 1120 g of a second-stage monomer emulsion of the under-mentioned composition was continuously fed over a period of 60 minutes for seeded polymerization.

Second-stage monomer emulsion

MMA	594.0 g
EA	66.0 g
E950, 10% aqueous solution	220.0 g
DIW	440.0 g

The reaction mixture was heated to 80°C and kept for one hour then, cooled and filtered through a 300-mesh stainless steel sieve to give a core-shell polymer latex.

This latex was frozen at -15°C and filtered through a glass filter. The solid was then dried in a current of air at 60°C overnight to give core-shell polymer B.

Example 3 Production of core-shell polymer C

A 2-liter polymerization vessel equipped with a reflux condenser was charged with 600 g of DIW and 20 g of a 10% aqueous solution of YX500 and the mixture was stirred under a nitrogen stream and heated to 35°C. A monomer mixture of 35 g of VAc and 15 g of EA was added to the above mixture and dispersed for 10 minutes. 12 g of a 3% aqueous solution of H₂O₂ and 12 g of a 2% aqueous solution of VC were added for polymerization of seed latex.

665 g of a first-stage monomer mixture of the under-mentioned composition was mixed with 135 g of a 10% aqueous solution of YX500 and 95 g of DIW. Then, the mixture was fed to the reaction mixture over a period of 240 minutes, followed by 72.5 g of a 3% aqueous solution of H₂O₂ and 72.5 g of a 2% aqueous solution of VC were continuously fed over a period of 300 minutes for seeded polymerization. While the monomer solution was fed, the reaction temperature was kept at the range from 35°C to 40°C.

First-stage monomer	
BA	697.20 g
A1MA	1.40 g
BGA	1.40 g

The reaction mixture was kept for one hour at the same temperature after finish of feeding monomers, and was subject to the second-stage polymerization.

32.9 g of a 3% aqueous solution of H₂O₂ and 32.9 g of VC was fed to the reaction mixture over a period of 150 minutes, and 431 g of a second-stage monomer emulsion of the under-mentioned composition was continuously fed over a period of 90 minutes for seeded polymerization. While the monomer solution was fed, the reaction temperature was kept at the range from 35°C to 40°C.

Second-stage monomer emulsion	
MMA	253.8 g
EA	28.2 g
YX500 10% aqueous solution	47.0 g
DIW	102.0 g

The reaction mixture was kept for one hour at the same temperature, then, cooled and filtered through a 300-mesh stainless steel sieve to give a core-shell polymer latex.

This latex was frozen at -15°C and filtered through a glass filter. The solid was then dried in a current of air at 60°C overnight to give core-shell polymer C.

Example 4 Production of core-shell polymer D

A 5-liter autoclave was charged with 1,000g of DIW and 24g of a 10% aqueous solution of E950, and the mixture was stirred under a nitrogen stream and heated to 70°C. Fifty-six grams of a first-stage monomer mixture of the under-mentioned composition was added to the above mixture and dispersed for 10 minutes. Then, 135g of a 2% aqueous solution of V50 was added for polymerization of seed latex.

First-stage monomer	
Bd	784g
St	336g

The remaining 1,096g portion of the first-stage monomer mixture and the mixture of 100g of 10% aqueous solution of E950 and 680g of DIW were continuously fed over a period of 420 minutes for seeded polymerization.

Thirty-three grams of 2% aqueous solution of V50 was added and the reaction mixture was heated to 80°C and kept for two hours.

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Seven hundreds grams of DIW was slowly added and kept 70°C. Seventy-two grams of 2% aqueous solution of V50 was added and 480g of a second-stage monomer of the under-mentioned composition was continuously fed over a period of 90 minutes for seeded polymerization.

Second-stage monomer	
MMA	333.6g
St	144.0g
BGA	2.4g
DIW	102.0g

The reaction mixture was heated to 80°C and kept for one hour then, cooled and filtered through a 300-mesh stainless steel sieve to give a core-shell polymer latex.

This latex was frozen at -15°C and filtered through a glass filter. The solid was then dried in a current of air at 60°C overnight to give core-shell polymer D.

Examples 5 to 10 Production of core-shell polymers E to J

According to the method of Example 2, core-shell polymers E to J were produced using the compositions mentioned below in Table 1.

Example 11 Production of POM resin composition (1)

A mixture of 90 parts of POM copolymer resin (TENAC C3510, Asahi Chemical Industry) and 10 parts of core-shell polymer A (Example 1) was dried to a water content of 0.03% or less and using a twin-screw extruder (PCM-30, Ikegai Iron Work's), the mixture was extruded at a cylinder temperature of 200°C and a die head temperature of 200°C to give pellets of POM resin composition (1).

Examples 12 to 24 Production of POM resin compositions (2) - (14)

In the same manner as Example 11, POM resin compositions (2) - (14) were produced according to the formulas shown in Table 2.

Example 25 Production of POM resin composition (15)

Using 80 parts of POM homopolymer resin (TENAC 3010, Asahi Chemical Industry) and 20 parts of core-shell polymer A (Example 1), the procedure of Example 12 was followed to give POM resin composition (15) according to the formula shown in Table 2.

Comparative Example 1 Production of POM resin composition (16)

Using an impact modifier L (KM330, Rohm & Haas Co.) and POM copolymer resin, POM resin composition (16) was produced and pellets were then prepared.

Comparative Example 2 Production of POM resin composition (17)

Using an urethane elastomer as an impact modifier M (T-680, Takeda-Badisch Urethane Industries Ltd.) and POM copolymer resin, POM resin composition (17) was produced and pellets were prepared.

Comparative Example 3 Production of core-shell polymer N and POM resin composition (18)

A 5-liter polymerization vessel equipped with a reflux condenser was charged with 1125 g of DIW, 50 g of a 1% aqueous solution of NP and 100 g of a 1% aqueous solution of SBC and the mixture was heated to 70°C with stirring under a nitrogen stream.

Then, 100 g of a first-stage monomer mixture of the under-mentioned composition was added and dispersed over a period of 10 minutes and 200 g of a 2% aqueous solution of SPS was then added for polymerization of seed latex.

First-stage monomer	
BA	1992 g
A1MA	4.0 g
BGA	4.0 g

Then, the remaining 1900 g portion of the first-stage monomer mixture was mixed with 1125 g of 1% aqueous solution of NP and 100 g of 1% aqueous solution of SBC and the resulting monomer emulsion was continuously fed to the reaction vessel over a period of 120 minutes for seeded emulsion polymerization.

The reaction mixture was heated to 90°C and kept for one hour, then cooled to 70°C. The second-stage polymerization was initiated at 70°C.

Thus, 50 g of 2% aqueous solution of SPS was added and 775 g of a second-stage monomer emulsion of the under-mentioned composition was continuously fed over a period of 45 minutes for seeded emulsion polymerization.

Second-stage monomer emulsion	
MMA	450.0 g
EA	50.0 g
NP, 1% aqueous solution	225.0 g
SBC, 1% aqueous solution	50.0 g

The reaction mixture was heated to 90°C and kept for one hour, and cooled and filtered through a 300-mesh stainless steel sieve to give a core-shell polymer latex.

The above latex was frozen at -15°C, filtered through a glass filter and dried in a current of air at 60°C overnight to give core-shell polymer N.

Using this core-shell polymer N and POM copolymer resin, POM resin composition (18) was produced and pellets were prepared.

Comparative Example 4 Production of core-shell polymer K

According to the method of Example 2, core-shell polymer K was produced using the composition mentioned below in Table 1.

Comparative Example 5 Production of POM resin composition (19)

In the same manner as Example 11, POM resin compositions (19) was produced according to the formulas shown in Table 2. But the melt-blended resin composition was colored as yellow and its thermal stability was very poor.

[Impact strength test of resin compositions]

Each of resin compositions (1) to (15) and (17) was dried at 120°C for 4 hours and, then, molded with an injection molding machine (TS-100, Nissei Resin) at a cylinder and nozzle temperature of 200°C. The molding was notched by machining to prepare Izod impact strength testpieces, 3.2 mm thick and 6.4 mm thick, according to JIS K7110. The impact values of these testpieces at 23°C were measured by the procedure directed in JIS K7110.

POM resin compositions (16) and (18) (Comparative Examples 1 and 3) were found to be not melt-blendable because POM resin was decomposed terribly, while POM resin composition (18) (Comparative Example 2) was unsatisfactory in thermal stability and fluidity.

The blending results are shown in Table 2.

[Determination of anion in core-shell polymers]

An amount of sulfate anion was determined by the method which comprises stirring 5 g of core-shell polymers in 20 ml of distilled water for 3 hours at room temperature, filtrating the core-shell polymer solution to obtain filtrate, dividing the filtrate into two parts of the same volume, adding 0.1 ml of 1% barium chloride aqueous solution into one part of the filtrate and comparing the solution with another filtrate.

The sulfate anion in the core-shell polymers A to J were not detected. The core-shell polymer A to J substantially contain no sulfate anion.

The precipitation yielded by sulfate anion contained in the core-shell polymer L and N were observed.

An amount of halogen anion was determined by the method which comprises stirring 5 g of core-shell polymers in 20 ml of distilled water for 3 hours at room temperature, filtrating the core-shell polymer solution to obtain filtrate, dividing the filtrate into two parts of the same volume, adding 0.5 ml of 0.1 N silver nitrate aqueous solution into one

part of the filtrate and comparing the solution with another filtrate.

The halogen anion in the core-shell polymers A to J were not detected. The core-shell polymer A to J substantially contain no anion.

It was known that the core-shell polymer K has metal carboxylate at the detectable amount calculated according to an amount of surfactant to be used for producing it.

[Measurement of the ratio of weld and non-weld elongation]

The ratio of weld and non-weld elongation was determined, according to JIS K 7113 by the ratio of the tensile elongation using the specimen which has two gate points at the both edges and the tensile elongation using the specimen which has one gate point at the edge.

[Weatherability Test]

The color difference between non-exposed and exposed injection molded specimen by the Sunshine Super Long-Life Weather Meter® (Suga Test Instruments) was measured using Σ80 Color Measuring System® (Nippon Denshoku Kogyo).

Table 1 Compositions of Core-Shell Polymers

Ex. No.	1	2	3	4	5	6	7	8	9	10	Comp. Ex. 3	Comp. Ex. 4
Impact Modifier	A	B	C	D	E	F	G	H	I	J	N	K
<u>Core</u>												
BA	69.72	69.72	66.57	-	79.44	-	74.475	69.51	69.51	69.51	79.68	69.51
BGA	0.14	0.14	0.13	-	0.16	0.15	0.15	0.14	0.14	0.14	0.16	0.14
ADMA	0.14	0.14	0.13	-	0.40	0.375	0.375	0.35	0.35	0.35	0.16	0.35
Bd	-	-	-	56.0	-	-	-	-	-	-	-	-
St	-	-	-	14.0	-	-	-	-	-	-	-	-
EA	-	-	3.52	-	-	-	-	-	-	-	-	-
2EHA	-	-	-	-	-	74.475	-	-	-	-	-	-
VAC	-	-	1.51	-	-	-	-	-	-	-	-	-
Core/MID/Shell	70//30	70//30	72//28 70//30 (71.86)	80/0.5//20	75//25 75//20//5	70//30	70//30	70//30	70//30	70//30	80//20	70//30

Table 1 (Continued)

Ex. No.	1	2	3	4	5	6	7	8	9	10	Comp. Ex.3 N	Comp. Ex.4 K
Imprct Modifier	A	B	C	D	E	F	G	H	I	J		
<u>Intermediate Phase (MID)</u>												
GMA	-	-	-	-	0.5	-	-	-	-	-	-	-
MMA	-	-	-	-	-	-	16.96	-	-	-	-	-
EA	-	-	-	-	-	-	3.0	-	-	-	-	-
BGA	-	-	-	-	-	-	0.04	-	-	-	-	-
APMA	-	-	-	-	-	-	-	-	-	-	-	-
<u>Shell</u>												
MMA	27.0	27.0	25.33	20.85	16.96	21.20	3.99	25.44	25.44	25.44	18.0	25.44
EA	3.0	3.0	2.81	-	3.0	3.75	0.75	4.50	4.50	4.50	2.0	4.50
BGA	-	-	-	0.15	0.04	0.05	0.01	0.06	0.06	0.06	-	0.06
HEMA	-	-	-	-	-	-	0.25	-	-	-	-	-
St	-	-	-	9.0	-	-	-	-	-	-	-	-

Table 1 (Continued)

Ex. No.	1	2	3	4	5	6	7	8	9	10	Comp. Ex. 3	Comp. Ex. 4
Impact Modifier	A	B	C	D	E	F	G	H	I	J	N	K
Surfactant	E950	E950	YX500	E950	E950	E950	E950	S-40	LT221	EPN	NP	OS
Polymerization Initiator	V601	V50	H ₂ O ₂ /VC	V50	V50	V50	V50	V50	V50	V50	SPS	V50

Table 2

Examples	Ex.11	Ex.12	Ex.13	Ex.14	Ex.15	Ex.16	Ex.17	Ex.18	Ex.19	Ex.20	Ex.21	Ex.22	Ex.23	Ex.24	Ex.25
Resin composition (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
Impact Modifier (A)	(A)	(A)	(A)	(A)	(A)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)	(K)	(L)
Ratio of POM to Impact Modifier	90/10	80/20	70/30	60/40	50/50	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20
Impact Modifier	90/10	80/20	70/30	60/40	50/50	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20
Izod impact	90/10	80/20	70/30	60/40	50/50	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20
[kJ/m ² (kgf·cm/cm)]															
3.2 mm thick	9.2	11.3	11.5	14.0	15.1	10.8	10.4	15.0	11.5	11.7	13.1	10.6	10.3	10.4	13.2
(9.4)	(11.5)	(11.7)	(14.3)	(15.4)	(11.0)	(10.6)	(10.6)	(15.3)	(11.7)	(11.9)	(13.3)	(10.8)	(10.5)	(10.6)	(13.5)
6.4 mm thick	9.2	10.3	9.6	11.0	12.8	8.9	8.0	12.2	8.0	11.0	9.1	8.5	8.6	8.2	11.4
(9.4)	(10.5)	(9.8)	(11.2)	(13.0)	(9.1)	(8.2)	(8.2)	(12.4)	(8.2)	(11.2)	(9.3)	(8.7)	(8.8)	(8.4)	(11.6)
Ratio of weld and non-weld elongation (Z)	-	-	-	-	-	120	-	-	80	-	95	-	-	-	-
Color difference (ΔE)	2.61	2.28	1.12	1.05	0.96	2.17	2.15	-	-	-	-	-	-	-	-

Comparative Examples	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.5	Control
Resin composition (16)	(17)	(18)	(19)	(20)	(21)
Impact Modifier	L	M	N	K	None
Izod impact					

[kJ/m² (kgf·cm/cm)]

3.2 mm thick	-	12.2	-	-	4.4
-	-	(12.4)	-	-	(4.5)
6.4 mm thick	-	9.4	-	-	5.4
-	-	(9.6)	-	-	(5.5)
Ratio of weld and non-weld elongation (Z)	-	<0.6	-	-	55
Color difference (ΔE)	-	16.54	-	-	2.96

(Note) Control: Pellets of POM copolymer resin alone

Claims

1. A method of producing a core-shell polymer by seeded emulsion polymerization which method is performed by

- (a) feeding a mixture of a conjugated diene or a C₂₋₈ alkyl acrylate or a mixture thereof and/or a monomer copolymerizable therewith and a nonionic surfactant in water into a reactor, adding a polymerization initiator which liberates neutral radicals and emulsion polymerizing said mixture to obtain a rubbery polymer core,
 (b) feeding a mixture of a methyl methacrylate and a monomer copolymerizable therewith and a nonionic surfactant into the reactor, adding a polymerization initiator which liberates neutral radicals and emulsion polymerizing composition to obtain a core-shell polymer;

wherein the glass transition temperature of the rubbery core phase is not more than -30 °C and the glass transition temperature of the glassy shell phase is not less than 60 °C.

2. The method of producing a core-shell polymer as claimed in claim 1, wherein the polymerization initiator is an initiator of the azo type.

3. The method of producing a core-shell polymer as claimed in claim 2, wherein the initiator of the azo type is azobis (isobutyronitrile), dimethyl 2,2'-azobis(isobutyrate) or 2,2'-azobis(2-amidinopropane)·2HCl.

4. The method of producing a core-shell polymer as claimed in claim 1, wherein the polymerization initiator is an initiator of the peroxide type.

5. The process of claim 1, wherein the monomer forming the rubbery polymer is a conjugated diene or a C₂₋₈ alkylacrylate, or a mixture thereof.

6. The process of claim 1 or 5, wherein in the step (a) polymerization the seed monomer is a conjugated diene and/or C₂₋₈ alkyl acrylate copolymerized with other comonomers selected from aromatic vinyl or vinylidene monomers, vinyl or vinylidene cyanides and alkyl methacrylates.

7. A core-shell polymer obtainable by seeded emulsion polymerizing a core of a conjugated diene or a C₂₋₈ alkylacrylate or a mixture thereof and a shell of methyl methacrylate and a monomer copolymerizable therewith according to the method of claim 1 comprising a rubbery polymer core and a glassy polymer shell characterized in that it has no detectable anion by

(a) the method which comprises stirring 5 g of the core-shell polymer in 20 ml of distilled water for 3 hours at room temperature, adding 0.1 ml of 1% barium chloride aqueous solution to the extracted sample solution, and observing whether precipitation appeared or not, or

(b) the method which comprises stirring 5 g of the core-shell polymer in 20 ml of distilled water for 3 hours at room temperature, adding 0.5 ml of 0.1 N silver nitrate aqueous solution to the extracted sample solution, and observing whether precipitation appeared or not.

8. The core-shell polymer as claimed in claim 7, wherein a transition temperature of the rubbery polymer is not over -30 °C.

9. The core-shell polymer as claimed in claim 7, wherein a transition temperature of the glassy polymer is not less than 60 °C.

10. The core-shell polymer as claimed in claim 7, wherein an amount of the rubbery polymer core is from 50 to 90 weight% per the whole core-shell polymer.

11. The core-shell polymer as claimed in claim 7, wherein an amount of the glassy polymer is from 10 to 50 weight% per the whole core-shell polymer.

12. A polyoxymethylene resin composition comprising the core-shell polymer as claimed in claim 7 or obtained by the method of claims 1-6.

13. A molded article made of the resin composition as claimed in claim 12.

14. Use of the core-shell polymer of claim 7 or obtained by the method of claims 1 to 6 as an impact modifier for polyoxymethylene resins.

5 Patentansprüche

1. Verfahren zur Herstellung eines Kern-Hülle-Polymers durch Keimbildungs-Emulsionspolymerisation, wobei das Verfahren durchgeführt wird durch

(a) Einleiten eines Gemischs aus einem konjugierten Dien oder einem C₂₋₈-Alkylacrylat oder einem Gemisch davon und/oder einem damit copolymerisierbaren Monomer und einem nichtionischen Tensid in Wasser in einen Reaktor, Hinzufügen eines Polymerisationsinitiators, der neutrale Radikale freisetzt, und Emulsionspolymerisieren des Gemischs, so daß man einen kautschukartigen Polymerkern erhält;

(b) Einleiten eines Gemischs aus Methylmethacrylat und einem damit copolymerisierbaren Monomer und einem nichtionischen Tensid in den Reaktor, Hinzufügen eines Polymerisationsinitiators, der neutrale Radikale freisetzt, und Emulsionspolymerisieren der Zusammensetzung, so daß man ein Kern-Hülle-Polymer erhält;

wobei die Glasübergangstemperatur der kautschukartigen Kernphase nicht mehr als -30°C beträgt und die Glasübergangstemperatur der glasartigen Hüllenphase nicht mehr als 60°C beträgt.

2. Verfahren zur Herstellung eines Kern-Hülle-Polymers gemäß Anspruch 1, wobei der Polymerisationsinitiator ein Initiator des Azotyps ist.

3. Verfahren zur Herstellung eines Kern-Hülle-Polymers gemäß Anspruch 2, wobei es sich bei dem Initiator des Azotyps um Azobis(isobutyronitril), Dimethyl-2,2'-azobis(isobutyrat) oder 2,2'-Azobis(2-amidinopropan)-2HCl handelt.

4. Verfahren zur Herstellung eines Kern-Hülle-Polymers gemäß Anspruch 1, wobei der Polymerisationsinitiator ein Initiator des Peroxidtyps ist.

5. Verfahren gemäß Anspruch 1, wobei es sich bei dem das kautschukartige Polymer bildenden Monomer um ein konjugiertes Dien oder ein C₂₋₈-Alkylacrylat oder ein Gemisch davon handelt.

6. Verfahren gemäß Anspruch 1 oder 5, wobei das Keimbildungsmonomer in der Polymerisation von Schritt (a) ein konjugiertes Dien und/oder C₂₋₈-Alkylacrylat ist, das mit anderen Comonomeren, die aus aromatischen Vinyl- oder Vinylidenmonomeren, Vinyl- oder Vinylidencyaniden und Alkylmethacrylaten ausgewählt sind, copolymerisiert ist.

7. Kern-Hülle-Polymer, das durch eine Keimbildungs-Emulsionspolymerisation eines Kerns aus einem konjugierten Dien oder einem C₂₋₈-Alkylacrylat oder einem Gemisch davon und einer Hülle aus Methylmethacrylat und einem damit copolymerisierbaren Monomer nach dem Verfahren gemäß Anspruch 1 erhältlich ist und einen kautschukartigen Polymerkern und eine glasartige Polymerhülle enthält, dadurch gekennzeichnet, daß es kein Anion enthält, das nachweisbar wäre durch

(a) das Verfahren, das das Rühren von 5 g des Kern-Hülle-Polymers in 20 ml destilliertem Wasser während 3 Stunden bei Raumtemperatur, das Hinzufügen von 0,1 ml 1%iger wäßriger Bariumchloridlösung zu der extrahierten Probelösung und das Beobachten, ob eine Fällung auftritt oder nicht, umfaßt, oder

(b) das Verfahren, das das Rühren von 5 g des Kern-Hülle-Polymers in 20 ml destilliertem Wasser während 3 Stunden bei Raumtemperatur, das Hinzufügen von 0,5 ml 0,1 N wäßriger Silbernitratlösung zu der extrahierten Probelösung und das Beobachten, ob eine Fällung auftritt oder nicht, umfaßt.

8. Kern-Hülle-Polymer gemäß Anspruch 7, wobei die Übergangstemperatur des kautschukartigen Polymers nicht über -30°C liegt.

9. Kern-Hülle-Polymer gemäß Anspruch 7, wobei die Übergangstemperatur des glasartigen Polymers nicht weniger als 60°C beträgt.

10. Kern-Hülle-Polymer gemäß Anspruch 7, wobei die Menge des kautschukartigen Polymerkerns 50 bis 90 Gew.-% des gesamten Kern-Hülle-Polymers beträgt.

11. Kern-Hülle-Polymer gemäß Anspruch 7, wobei die Menge des glasartigen Polymers 10 bis 50 Gew.-% des gesamten Kern-Hülle-Polymers beträgt.
12. Polyoxymethylen-Harzzusammensetzung, die das Kern-Hülle-Polymer gemäß Anspruch 7 oder eines, das nach dem Verfahren von Anspruch 1 bis 6 erhalten wurde, umfaßt.
13. Formkörper, der aus der Harzzusammensetzung gemäß Anspruch 12 hergestellt wurde.
14. Verwendung des Kern-Hülle-Polymer gemäß Anspruch 7 oder von einem, das nach dem Verfahren von Anspruch 1 bis 6 erhalten wurde, als Schlagzähmacher für Polyoxymethylenharze.

Revendications

1. Procédé de production d'un polymère de type coeur/enveloppe, par polymérisation en émulsionensemencée, lequel procédé est mis en oeuvre ainsi :

a) on envoie dans un réacteur un mélange contenant, dans de l'eau, un diène conjugué ou un acrylate d'alkyle en C_{2-8} , ou un mélange de tels composés, et/ou un monomère copolymérisable avec eux, ainsi qu'un tensioactif non-ionique, on ajoute un amorceur de polymérisation qui libère des radicaux neutres, et l'on fait polymériser en émulsion ledit mélange, ce qui donne un polymère caoutchouteux de coeur ;

b) on envoie dans le réacteur un mélange contenant du méthacrylate de méthyle et un monomère copolymérisable avec ce composé, ainsi qu'un tensioactif non-ionique, on ajoute un amorceur de polymérisation qui libère des radicaux neutres, et l'on fait polymériser en émulsion la composition, ce qui donne un polymère coeur/enveloppe ;

la température de transition vitreuse de la phase caoutchouteuse de coeur ne valant pas plus de $-30^{\circ}C$ et la température de transition vitreuse de la phase vitreuse d'enveloppe ne valant pas moins de $60^{\circ}C$.

2. Procédé de production d'un polymère de type coeur/enveloppe, conforme à la revendication 1, dans lequel l'amorceur de polymérisation est un amorceur de type azoïque.
3. Procédé de production d'un polymère de type coeur/enveloppe, conforme à la revendication 1, dans lequel l'amorceur de type azoïque est de l'azo-bis(isobutyronitrile), du 2,2'-azo-bis(isobutyrate) de diméthyle ou du dichlorhydrate de 2,2'-azo-bis(2-amidinopropane).
4. Procédé de production d'un polymère de type coeur/enveloppe, conforme à la revendication 1, dans lequel l'amorceur de polymérisation est un amorceur de type peroxyde.
5. Procédé conforme à la revendication 1, dans lequel le monomère qui forme le polymère caoutchouteux est un diène conjugué ou un acrylate d'alkyle en C_{2-8} , ou un mélange de tels composés.
6. Procédé conforme à la revendication 1 ou 5, dans lequel, au cours de l'étape (a) de polymérisation, le monomère des germes est un diène conjugué et/ou un acrylate d'alkyle en C_{2-8} , copolymérisé avec d'autres comonomères choisis parmi les monomères vinyl-aromatiques, les monomères vinylidène-aromatiques, les cyanures de vinyle ou de vinylidène, et les méthacrylates d'alkyle.
7. Polymère de type coeur/enveloppe, comportant un coeur de polymère caoutchouteux et une enveloppe de polymère vitreux, qu'on peut obtenir en formant par polymérisation en émulsionensemencée, selon le procédé indiqué dans la revendication 1, un coeur à partir d'un diène conjugué, d'un acrylate d'alkyle en C_{2-8} ou d'un mélange de tels composés, et une enveloppe à partir de méthacrylate de méthyle et d'un monomère copolymérisable avec ce composé, ledit polymère étant caractérisé en ce qu'il ne contient pas d'anions qui soient détectables

a) par une méthode qui comporte le fait de brasser pendant 3 heures, à la température ambiante, 5 g du polymère coeur/enveloppe dans 20 ml d'eau distillée, le fait d'ajouter à la solution résultant de cette extraction de l'échantillon 0,1 ml de solution aqueuse à 1 % de chlorure de baryum, et le fait de voir s'il se forme ou non un précipité, ou

b) par une méthode qui comporte le fait de brasser pendant 3 heures, à la température ambiante, 5 g du

polymère coeur/enveloppe dans 20 ml d'eau distillée, le fait d'ajouter à la solution résultant de cette extraction de l'échantillon 0,5 ml de solution aqueuse 0,1 N de nitrate d'argent, et le fait de voir s'il se forme ou non un précipité.

- 5 8. Polymère de type coeur/enveloppe, conforme à la revendication 7, dans lequel la température de transition vitreuse du polymère caoutchouteux ne vaut pas plus de -30 °C.
9. Polymère de type coeur/enveloppe, conforme à la revendication 7, dans lequel la température de transition vitreuse du polymère vitreux ne vaut pas moins de 60 °C.
- 10 10. Polymère de type coeur/enveloppe, conforme à la revendication 7, dans lequel la quantité de polymère caoutchouteux du coeur représente de 50 à 90 % du poids de tout le polymère coeur/enveloppe.
11. Polymère de type coeur/enveloppe, conforme à la revendication 7, dans lequel la quantité de polymère vitreux
- 15 11. Polymère de type coeur/enveloppe, conforme à la revendication 7, dans lequel la quantité de polymère vitreux représente de 10 à 50 % du poids de tout le polymère coeur/enveloppe.
12. Composition de résine de poly(oxyméthylène) comportant un polymère de type coeur/enveloppe, conforme à la revendication 7 ou obtenu selon un procédé conforme à l'une des revendications 1 à 6.
- 20 13. Pièce moulée en une composition de résine conforme à la revendication 12.
14. Emploi d'un polymère de type coeur/enveloppe, conforme à la revendication 7 ou obtenu selon un procédé conforme à l'une des revendications 1 à 6, comme agent améliorant la résistance au choc dans des résines de poly(oxyméthylène).
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